

	L #	Hits	Search Text	DBs	Time Stamp
1	L1	278	(transparent near2 conductive) and crystalliz\$8 and photovoltaic	US- PGPUB; USPAT; EPO; JPO; DERWEN T; IBM_TD B	2005/02/25 09:05
2	L2	219	((transparent near2 conductive) and crystalliz\$8 and photovoltaic) and rate	US- PGPUB; USPAT; EPO; JPO; DERWEN T; IBM_TD B	2005/02/25 09:07
3	L3	22813	photovoltaic	US- PGPUB; USPAT; EPO; JPO; DERWEN T; IBM_TD B	2005/02/25 09:07
4	L4	455257	flow\$4 near2 rate\$3	US- PGPUB; USPAT; EPO; JPO; DERWEN T; IBM_TD B	2005/02/25 09:07

	L #	Hits	Search Text	DBs	Time Stamp
5	L5	254066	"zinc oxide" or "tin oxide" or "indium oxide" or "titanium oxide" or ZnO or TiO or InO	US- PGPUB; USPAT; EPO; JPO; DERWEN T; IBM_TD B	2005/02/25 09:07
6	L6	3442	L3 and L5	US- PGPUB; USPAT; EPO; JPO; DERWEN T; IBM_TD B	2005/02/25 09:07
7	L7	698	L6 and L4	US- PGPUB; USPAT; EPO; JPO; DERWEN T; IBM_TD B	2005/02/25 09:07
8	L11	513	(438/486).CCLS.	US- PGPUB; USPAT; USOCR; EPO; JPO; DERWEN T; IBM_TD B	2005/02/25 09:07

	L #	Hits	Search Text	DBs	Time Stamp
9	L8	456	L7 and (@ad<"20010201")	US- PGPUB; USPAT; EPO; JPO; DERWEN T; IBM_TD B	2005/02/25 09:07
10	L9	459	(438/478) .CCLS.	US- PGPUB; USPAT; USOCR; EPO; JPO; DERWEN T; IBM_TD B	2005/02/25 09:08
11	L12	291	(438/485) .CCLS.	US- PGPUB; USPAT; USOCR; EPO; JPO; DERWEN T; IBM_TD B	2005/02/25 10:36
12	L13	513	(438/486) .CCLS.	US- PGPUB; USPAT; USOCR; EPO; JPO; DERWEN T; IBM_TD B	2005/02/25 11:07

600 nm and
tan θ . in which θ is an angle of inclination in the
range of about
0.07 to 0.20. Further, a metal electrode, for example, in the shape
of a comb,
may be formed as a collector on the electrode provided on the n-layer
or the
p-layer located at the top. The metal electrode may be formed of the
same
conductive materials as mentioned above.

Detail Description Paragraph - DETX (47):

[0081] On the transparent conductive film 22, a thin film of p-
type silicon
(a p-layer) 23 containing a crystalline component was deposited to a
thickness
of 25 nm by RF plasma enhanced CVD method at 13 MHz under gas flow
rates of 4
sccm for SiH₄, 0.1 sccm for B₂H₆ and 40 sccm for
H₂, a
substrate temperature of 140.degree. C., an applied power of 25 W
and a
pressure of 27 Pa. As shown in Table 3, where the p-layer was
deposited to a
thickness of 500 nm as a single layer on the glass substrate, the
crystal
fraction thereof was 0.58 and the integrated intensity ratio of the
X-ray
diffraction peak at (220) to that at (111) was 11. The concentration
of boron
in the p-layer was 0.5 atom % according to a measurement by secondary
ion mass
spectroscopy (SIMS).

Detail Description Paragraph - DETX (48):

[0082] Then, on the p-layer 23, a thin intrinsic silicon film (an
i-layer)
24 containing a crystalline component was deposited to a thickness of
1.5 μ m
by RF plasma enhanced CVD method at 13 MHz under gas flow rates of 5
sccm for
SiH₄ and 90 sccm for H₂, a substrate temperature of
200.degree. C.,
an applied power of 100 W and a pressure of 40 Pa. The deposition
rate of the
film was 36 nm/min. As shown in Table 3, when the i-layer was
deposited to a
thickness of 500 nm as a single layer on the glass substrate, the
crystal
fraction was 0.82 and the integrated intensity ratio of the X-ray

diffraction peak at (220) to that at (111) was 0.8. Further, when the i-layer was deposited to a thickness of 1.5 g m as a single layer on the glass substrate, the crystal fraction thereof was 0.82 and the integrated intensity ratio of the X-ray diffraction peak at (220) to that at (111) was 0.9. That is, where the i-layer used in this example was deposited as a single layer, it did not show a preferential crystal orientation but showed a so-called random orientation.

Detail Description Paragraph - DETX (49):

[0083] On the i-layer 24, a thin film of n-type silicon (an n-layer) 25 was deposited to a thickness of 15 nm by RF plasma enhanced CVD method under gas flow rates of 4 sccm for SiH.sub.4, 0.01 sccm for PH.sub.3 and 100 sccm for H.sub.2, a substrate temperature of 190.degree. C., an applied power of 25 W and a pressure of 33 Pa.

Detail Description Paragraph - DETX (52):

[0086] On the n-layer 25 a ZnO film of 50 nm thick was formed by sputtering as a back reflective layer 26 and an Ag film of 400 nm thick was formed by sputtering as a back electrode 27.

Detail Description Paragraph - DETX (53):

[0087] Characteristics of the thus manufactured thin film solar cell of a superstrate type in which light enters from the glass substrate 21 were checked as shown in Table 4. The obtained solar cell element had an efficient irradiation area of 1 cm.sup.2. The photovoltaic conversion efficiency was measured after irradiating pseudo-sunbeam of AM 1.5 and 100 mW/cm.sup.2 at 50.degree. C. for 500 hours to verify deterioration of the solar cell element through light irradiation. The measured photovoltaic conversion efficiency was equal to that before 500 hours, and thus deterioration was not observed.

Detail Description Paragraph - DETX (56):

[0089] In Example 2, the i-layer 24 was formed under the same conditions described in Example 1 except that the applied power of 50 W was employed. The rate of the film formation was 18 nm/min. When the i-layer was formed to a thickness of 1.5 μm as a single layer on the glass substrate, the crystal fraction thereof was 0.78 and the integrated intensity ratio of the X-ray diffraction peak at (220) to that at (111) was 6.4. In Example 3, the i-layer 24 was formed under the same conditions as Example 2 except that the gas flow rate of SiH_4 was changed to 3 sccm. The rate of the film formation was 12 nm/min. When the i-layer was formed to a thickness of 1.5 μm as a single layer on the glass substrate, the crystal fraction thereof was 0.80 and the integrated intensity ratio of the X-ray diffraction peak at (220) to that at (111) was 4.2. Thus, the crystal properties of the single i-layer were varied. The i-layers of Examples 2 and 3 exhibited the crystal fraction nearly equal to that of the i-layer of Example 1 but had a preferential orientation in the direction of $\langle 110 \rangle$.

Detail Description Paragraph - DETX (57):

[0090] From Table 3, it is found that when the single i-layer exhibited the preferential crystal orientation, the pin junction also showed the preferential crystal orientation which was remarkably improved. Further, Table 4 shows that the photovoltaic conversion efficiency was more enhanced in the thin film solar cell including the pin junction with the thus improved preferential crystal orientation.

Detail Description Paragraph - DETX (61):

[0093] On a transparent conductive film 22, the p-layer 23 containing a crystalline component was deposited to a thickness of 25 nm by plasma enhanced CVD method at a VHF band frequency of 81 MHz under gas flow rates of

4 sccm for
SiH.sub.4, 0.1 sccm for B.sub.2H.sub.6 and 120 sccm for H.sub.2, a
substrate
temperature of 240.degree. C., an applied power of 25 W and a
pressure of 27
Pa.

Detail Description Paragraph - DETX (62):

[0094] From Table 3, it is found that enhancement of the
preferential
crystal orientation of the p-layer formed as a bottom layer allowed
enhancement
of the preferential crystal orientation of the pin junction.
Further, Table 4
shows that the photovoltaic conversion efficiency of the thin film
solar cell
including the pin junction with the thus enhanced preferential
crystal
orientation was more improved.

Detail Description Paragraph - DETX (63):

[0095] Even if the i-layer was formed under the conditions which
increase
the deposition rate while deteriorating the preferential crystal
orientation of
the i-layer as a single layer, the preferential crystal orientation
of the pin
junction was compensated by the use of the p-layer having a stronger
crystal
preferential crystal orientation as that of Example 4. Thus, the
thin film
solar cell having greater photovoltaic conversion efficiency was
manufactured.

Detail Description Paragraph - DETX (67):

[0098] Table 3 shows that when the p-layer formed as a bottom
layer showed
the preferential crystal orientation as seen in Example 6, the pin
junction
could have a preferential crystal orientation even if the i-layer had
a random
orientation when deposited as a single layer. However, as in
Comparative
Example 1, where the bottom p-layer showed the random orientation,
the pin
junction also exhibited the random orientation, so that the
photovoltaic
conversion efficiency of the thin film solar cell was deteriorated.

Detail Description Paragraph - DETX (82):

[0110] On a glass plate 31 of 3 mm thick, Ag was deposited to a thickness of 400 nm by sputtering as a back electrode 32 and then a ZnO film of 100 nm thick was formed thereon by sputtering as a back reflective layer 33.

Detail Description Paragraph - DETX (83):

[0111] On the back reflective layer 33, a thin film of p-type silicon (a p-layer) 34 containing a crystalline component was deposited to a thickness of 25 nm by RF plasma enhanced CVD at 13 MHz under gas flow rates of 4 sccm for SiH.sub.4, 0.1 sccm for B.sub.2H.sub.6 and 40 sccm for H.sub.2, a substrate temperature of 140.degree. C. and a pressure of 27 Pa (the conditions for Example 1).

Detail Description Paragraph - DETX (84):

[0112] Then, on the p-layer 34, a thin film of intrinsic silicon (an i-layer) 35 containing a crystalline component was deposited to a thickness of 1.5 .mu.m by RF plasma enhanced CVD at 13 MHz under gas flow rates of 5 sccm for SiH.sub.4 and 90 sccm for H.sub.2, a substrate temperature of 200.degree. C., an applied power of 50 W and a pressure of 40 Pa (the conditions for Example 2).

Detail Description Paragraph - DETX (85):

[0113] On the i-layer 35, a thin film of n-type silicon (an n-layer) 36 was deposited to a thickness of 15 nm by RF plasma enhanced CVD under gas flow rates of 4 sccm for SiH.sub.4, 0.01 sccm for PH.sub.3 and 100 sccm for H.sub.2, a substrate temperature of 190.degree. C., an applied power of 25 W and a pressure of 33 Pa (the conditions for Example 1).

Detail Description Paragraph - DETX (89):

[0117] Characteristics of the thus manufactured solar cell element of a substrate type in which light enters from the transparent conductive film 37 were checked as shown in Table 9. The obtained solar cell element had an

efficient irradiation area of 1 cm.². The photovoltaic conversion efficiency was measured by irradiating the solar cell element with pseudo-sunbeam of AM 1.5 and 100 mW/cm.².

Detail Description Paragraph - DETX (90):

[0118] Table 9 shows that if the solar cell element was of a substrate type, high photovoltaic conversion efficiency was obtained by providing the p-layer having a greater preferential crystal orientation at the bottom.

Detail Description Paragraph - DETX (94):

[0121] On a transparent conductive film 22, a thin film of p-type silicon (a p-layer) 23 containing a crystalline component was deposited to a thickness of 25 nm by RF plasma enhanced CVD at 13 MHz under gas flow rates of 4 sccm for SiH.₄, 0.1 sccm for B.₂H.₆ and 40 sccm for H.₂, a substrate temperature of 140.degree. C., an applied power of 25 W and a pressure of 27 Pa. While maintaining the plasma, the B.₂H.₆ gas was stopped and a thin intrinsic silicon film (an i-layer) 24 containing a crystalline component was continuously deposited to a thickness of 1.5 μm under gas flow rates of 5 sccm for SiH.₄ and 90 sccm for H.₂, a substrate temperature of 200.degree. C., an applied power of 50 W and an inner pressure of 40 Pa (the conditions for Example 2).

Detail Description Paragraph - DETX (103):

[0129] On a transparent conductive film 22, a thin film of p-type silicon (a p-layer) 23 was deposited in the same manner as Example 1 and then the substrate is transported into a chamber for depositing a thin film of intrinsic silicon (an i-layer) 24. In the i-layer deposition chamber, plasma was generated for 30 seconds under a gas flow rate of 90 sccm for H.₂, a substrate temperature of 200.degree. C., an applied power of 50 W and a pressure of 40 Pa. Then, a thin film of intrinsic silicon (an i-layer) 24

containing a crystalline component was deposited on the p-layer 23 to a thickness of 1.5 μm under the same conditions as employed in Example 2.

Detail Description Paragraph - DETX (110):

[0136] Further, according to the present invention, a thin film solar cell is comprised of the p-layer, i-layer and n-layer formed as the pin junction on the substrate, the p-layer and the i-layer are silicon thin films each containing a crystalline component and the p-layer shows the integrated intensity ratio $I_{\text{sub.220}}/I_{\text{sub.111}}$ of the X-ray diffraction peak at (220) with respect to that at (111) greater than the integrated intensity ratio of the i-layer deposited as a single layer on a substrate. Accordingly, the pin junction includes the p-layer having a strong preferential crystal orientation as the bottom layer so that the high crystal fraction originally exhibited by a single i-layer and the strong preferential crystal orientation originally expressed by a single p-layer are both satisfied. Thus, a photoelectric conversion layer suitable for the stacking is obtained, which allows providing a thin film solar cell with high photovoltaic conversion efficiency. Further, according to the thus constructed thin film solar cell, the preferential crystal orientation of the i-layer is controlled by the p-layer formed at the bottom, so that the i-layer is formed under a greater discharge power and a smaller amount of diluent hydrogen, which improves the film deposition rate. Thus, productivity is highly improved.

Detail Description Paragraph - DETX (111):

[0137] In particular, the photovoltaic conversion efficiency is further enhanced in the cases where the p-layer, when deposited as a single layer to a thickness of 500 nm or more on a substrate, shows the preferential crystal orientation in the direction of $\langle 110 \rangle$, preferably, the

integrated
intensity ratio I_{220}/I_{111} of the X-ray diffraction peak at (220) with respect to that at (111) of 5 or more, where the pin junction formed on the substrate shows the integrated intensity ratio I_{220}/I_{111} of the X-ray diffraction peak at (220) with respect to that at (111) of 1 or more, preferably 5 or more, and where the p-layer, the i-layer and the n-layer are provided in this order on a transparent substrate and light enters from the transparent substrate.

Detail Description Paragraph - DETX (112):

[0138] Further, in the case where the p-layer and the i-layer are continuously formed by plasma enhanced CVD while varying the gas flow rate, the thin film solar cell of high efficiency is easily provided. Moreover, since the same film formation chamber can be used for forming the two layers, while separate chambers have been used in general, costs for equipment are reduced and throughput is improved.

Detail Description Paragraph - DETX (114):

[0140] Still according to the present invention, a thin film solar cell is comprised of a bottom layer and an upper layer formed directly on the bottom layer in a multi-layered pin junction or a multi-layered nip junction in which both layers contain a crystalline component, respectively, and the bottom layer shows a preferential orientation greater than a preferential orientation of the upper layer deposited as a single layer to the same thickness on a substrate. Alternatively, the upper layer, when deposited as a single layer on a substrate, shows the crystal fraction greater than that of the bottom layer and the stacked structure of the bottom layer and the upper layer in the pin junction or the nip junction shows the integrated intensity ratio I_{220}/I_{111} of the X-ray diffraction peak at (220) with respect to that at (111) of 5 or more. Therefore, the preferential orientation of the bottom layer is taken over by the upper layer. As a result, a high quality

photoelectric conversion layer is obtained, which allows obtaining a thin film solar cell of much greater photovoltaic conversion efficiency.

Detail Description Paragraph - DETX (115):

[0141] In particular, where the bottom layer is formed by plasma enhanced CVD utilizing VHF frequency band as an excitation frequency, the thin film solar cell with excellent photovoltaic conversion efficiency as mentioned above is easily manufactured.

Detail Description Paragraph - DETX (117):

[0143] Thus, if the thin film solar cell of the present invention is used as a solar cell module, a longlife solar cell module having high photovoltaic conversion efficiency which is stable over a long-term light irradiation is obtained since the photoelectric conversion layer of the thin film solar cell exhibits both of the high crystal fraction and the high preferential crystal orientation.

Detail Description Table CWU - DETL (4):

4 TABLE 4 Density of Photovoltaic short-circuit conversion
Open-circuit
current Fill efficiency voltage (V) (mA/cm.sup.2) Factor (%) Ex. 1
0.50 23.0
0.71 8.2 Ex. 2 0.52 23.8 0.74 9.2 Ex. 3 0.51 23.3 0.72 8.6 Ex. 4
0.51 23.5
0.72 8.6 Ex. 5 0.54 24.2 0.75 9.8 Ex. 6 0.48 22.8 0.70 7.7 Com.
0.42 22.5
0.62 5.9 Ex. 1

Detail Description Table CWU - DETL (6):

6 TABLE 6 Open- Density of Photovoltaic circuit short-circuit
conversion
voltage current Fill efficiency (V) (mA/cm.sup.2) factor (%) Ex. 1
0.50 23.0
0.71 8.2 Ex. 7 0.46 22.5 0.67 7.0 Ex. 8 0.49 23.0 0.70 7.9 Ex. 9
0.47 22.5
0.67 7.2 Ex. 10 0.46 22.1 0.65 6.6 Com. Ex. 1 0.42 22.5 0.62 5.9
Com. Ex. 2
0.38 19.3 0.52 3.8

Detail Description Table CWU - DETL (8):

8 TABLE 8 Open- Density of Photovoltaic circuit short-circuit

conversion

voltage current Fill efficiency (V) (mA/cm.sup.2) factor (%) Ex. 1
0.50 23.0
0.71 8.2 Ex. 11 0.46 24.2 0.67 7.5 Ex. 12 0.51 22.1 0.72 8.1 Ex.
13 0.50
21.2 0.71 7.5 Ex. 14 0.49 20.7 0.70 7.1 Ex. 15 0.48 20.2 0.68 6.7
Com. Ex.
3 0.37 22.1 0.51 4.2 Com. Ex. 4 0.47 19.3 0.60 5.4

Detail Description Table CWU - DETL (9):

9 TABLE 9 Preferential orientation of Crystal fraction Open-
circuit pin
junction of pin junction voltage I.sub.220/I.sub.111 Ic (Ic + Ia)
(V) Ex. 2
28 0.78 0.52 Ex. 16 26 0.78 0.51 Density of short- Photovoltaic
circuit
current conversion (mA/cm.sup.2) Fill factor efficiency Ex. 2 23.8
0.74 9.2
Ex. 16 23.2 0.72 8.5

Detail Description Table CWU - DETL (10):

10 TABLE 10 Preferential orientation of Crystal fraction Open-
circuit
pin junction of pin junction voltage I.sub.220/I.sub.111 Ic (Ic +
Ia) (V)
Ex. 2 28 0.78 0.52 Ex. 17 39 0.78 0.55 Density of short-
Photovoltaic
circuit current conversion (mA/cm.sup.2) Fill factor efficiency Ex.
2 23.8
0.71 9.2 Ex. 17 24.0 0.73 9.6

Detail Description Table CWU - DETL (11):

11 TABLE 11 Preferential orientation of pin Crystal fraction
Open-circuit
junction of pin junction voltage I.sub.220/I.sub.111 Ic (Ic + Ia)
(V) Ex. 2
28 0.78 0.52 Ex. 18 34 0.78 0.53 Density of Photovoltaic short-
circuit
conversion current efficiency (mA/cm.sup.2) Fill factor (%) Ex. 2
23.8
0.74 9.2 Ex. 18 23.8 0.75 9.5

Claims Text - CLTX (8):

7. A method of manufacturing a thin film solar cell according to
claim 1 or
2, wherein the p-layer and the i-layer are continuously formed by
plasma
enhanced CVD method while varying a gas flow rate.